

X-ray Charge Density of a New Covalent Network Anti-ferromagnetR. D. Poulsen¹, A. Bentien², M. Chevalier¹, and B. B. Iversen¹¹ Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.² Max Planck Institute for the Chemical Physics of Solids, Dresden, Germany

Beamline(s): X3A1

There has been an explosion of interest in metal-organic framework (MOF) systems.^[1] Recent highlights include nanoporous systems based on Zn centers coordinated by various di-carboxylate acids to form cubic host structures.^[2] By variation of the length of the acid linker incremental increases in pore sizes over a large range was achieved, and one member of this series of compounds exhibits the highest capacity for methane storage observed so far in a porous system.

Synthesis, multi-temperature structural characterization, magnetic property characterisation, heat capacity measurement and X-ray charge density analysis has been carried out on a new manganese based MOF. Contrary to many of the previously reported MOFs solvent molecules do not occupy the nanoporous voids but are coordinated directly to the magnetic manganese centers creating a crystalline system with much decreased structural disorder. Crystals of $\text{Mn}_3\text{O}_{14}\text{N}_2\text{C}_{34}\text{H}_{32}$, $(\text{Mn}_3(\text{BDC})_6(\text{DEF})_2)$, BDC = benzenedicarboxylate, DEF = diethylformamide) were obtained from synthesis procedures similar to the ones published for related non-magnetic MOFs.^[2] In Figure 1 the structure is shown based on 20 K synchrotron X-ray diffraction data obtained at beam line **X3A1** at **NSLS**. The macroscopic crystal shape directly reflects the skewed unit cell of the nanoporous framework, Figure 2. The inner part of the voids are occupied by the DEF solvent molecules, which are firmly bound at one coordination site to Mn(2). Even at room temperature the DEF molecule is only slightly disordered, and as the temperature is lowered to 20 K the disorder disappears.

Data sets were collected at 20 K and at room temperature at NSLS, whereas conventional data at many temperatures have been collected on a Bruker SMART CCD diffractometer at Department of Chemistry, University of Aarhus. The electron density of the system has been modelled at several temperatures with the multipole program XD, and experimental d-orbital populations have been extracted from the refined multipole populations of the two Mn centers. We have also carried out Bader topological analysis of the electron density, and used the topological properties to characterize the metal-ligand bonds.

[¹] M. O'Keeffe, M. Eddaoudi, H. Li., T. Reineke, O. M. Yaghi, J. Solid. State Chem. **2000**, 152, 3.

[²] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, Science 2002, 295, 469.

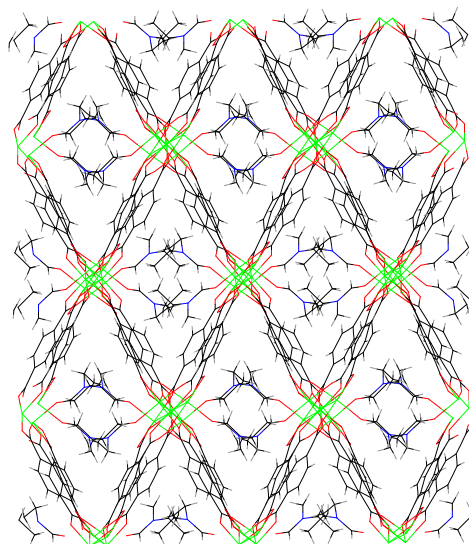
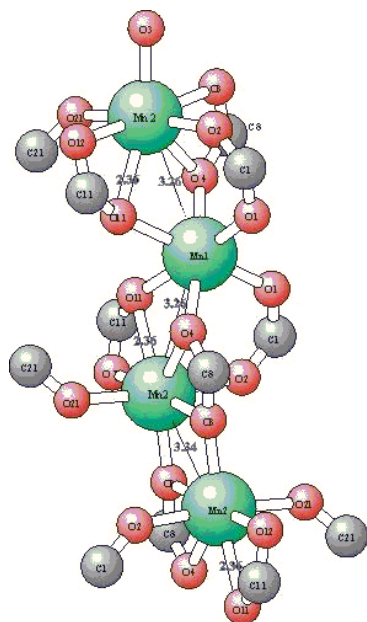


Figure 1. The molecular structure of $\text{Mn}_3(\text{BDC})_6(\text{DEF})_2$.

Figure 2. The nanoporous framework along b-axis